IN THE UNITED STATE PATENT AND TRADEMARK OFFICE

APPLICANT: Diane Elsie Hall	)	PATENT APPLICATION
APPLICATION NO.: 10/535,076	)	GROUP ART UNIT: 1797
CONFIRMATION NO.: 1916	)	EXAMINER: James C. Goloboy
FILED: May 13, 2005	)	Attorney Docket No.: BP 9861-00
FOR: Method of Reducing Particulate Emissions	)	

DECLARATION OF DIANE ELSIE HALL

UNDER 37 C.F.R. 1.31

Commissioner for Patents
P. O. Box 1450
Alexandria, Virginia
22313-1450

I, Diane Elsie Hall, hereby state as follows:

1. I am the inventor of above- indentified United States patent application number 10/535,076, and am familiar with the invention claimed therein.

2. The invention claimed in my above- identified U.S. patent application relates in general to a method of reducing the number of nucleation mode particles having diameters of between about 3 nm and 7 nm diameter in the emissions from a heavy duty diesel engine fitted with a catalytic regenerating particulate trap by the use of a lubricating oil having a low sulfur content of less than about 0.4 percent by weight and comprising ZDDP at a concentration of up to about 0.8 percent by weight and a fuel having a low sulfur content of less than about 50 ppm by weight.

DH

3. The United States Patent and Trademark Office has rejected all of pending Claims 16, 25, 26, 33 – 39, 41, and 53 of my above- identified U.S. patent application under 35 U.S.C. 103 (a), over Ritchie et al., U.S. Patent Application No. 2004/0048753 A1, in view of Cooper et al., U.S. Patent No. 4,902,487 and Twigg et al., U.S, Patent No. 6,294,141.

4. The filing date of the aforesaid Richie et al., U.S. Patent Application No. 2004/0048753 A1 is September 10, 2002.

5. I conceived the invention claimed in my above-identified U.S. patent application and actually reduced it to practice prior to September 10, 2002, as demonstrated by the following facts, all of which took place in the United Kingdom after January 1, 1996:

(a) Prior to September 10, 2002, I performed an investigation of the effect of fuel and lubricant sulfur content on the formation of nucleation particles in accordance with the Programme Objectives for this investigation, which are contained in two documents, both of which are dated prior to September 10, 2002. Copies of these two documents are attached hereto as Attachments A and B. The dates and confidential cost information have been redacted from these two documents. The details concerning the diesel engine and catalytic regenerating particulate trap (identified as "CRT"), the measurements of the sizes of the particles in the emissions, the sulfur levels of the fuels and lubricating oils and the combinations of (1) low sulfur fuel and low sulfur lubricating oil, (2) low sulfur fuel and high sulfur lubricating oil, and (3) high sulfur fuel and high sulfur lubricating oil to be tested, and the test procedure to be employed in the investigation are specified in the aforesaid Programme Objectives.

(b) Prior to September 10, 2002, I completed the aforesaid investigation and prepared and provided to my management a summary of the results of my aforesaid investigation, which summary is entitled "The effect of fuel sulfur levels on the formation of nucleation particles from trap equipped heavy duty Diesel engines." Prior to September 10, 2002, I sent an email to Nick Perkins and

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attached to that email electronic copies of the aforesaid Programme Objectives shown in Attachment A hereto and of my aforesaid summary. Copies of my aforesaid email to Nick Perkins and of my aforesaid summary are attached hereto as Attachment C. The dates have been redacted from my aforesaid email. The test materials, equipment and test procedures that are described in the aforesaid Programme Objectives were employed in my performance of the investigation and are also described on pages 5-7 of my above-described U.S. patent application. The results and my conclusions from my investigation are stated in my aforesaid summary and are also stated in my above-identified U.S. patent application. Except for some notations on the x-axis, the bar chart on the second page of my summary in Attachment C is the same bar chart that appears as Figure 2 in my above-identified U.S. patent application.

6. Therefore I believe that I conceived and actually reduced my aforesaid invention to practice in the U.K. prior to September 10, 2002 and subsequent to January 1, 1996.

7. In addition, I worked diligently in the ordinary course of work with Nick Perkins and Alex King of my employer's intellectual property law group regarding seeking patent protection for my aforesaid invention, as demonstrated by the following facts, all of which took place in the UK:

(a) On January 21, 2002, I discussed the results of my aforesaid investigation with Nick Perkins and confirmed that discussion with an email to Nick Perkins, dated January 22, 2002, a copy of which is attached hereto in aforesaid Attachment C. Electronic copies of the aforesaid Programme Objectives (Attachment A hereto) and the aforesaid summary of my results (Attachment C hereto) are attached to my email to Nick Perkins.

(b) On May 20, 2002, Alex King sent to me a first draft of a patent application for my aforesaid invention. The application was identified as being for Case No. 9861 (1) and was dated April 3, 2002. On this draft, Alex King had highlighted in red certain passages that he wanted to discuss further. A copy of

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Alex King's email to me and a copy of the electronic attachment to it are attached hereto as Attachment D. The disclosure in this first draft of a patent application substantially conforms to the disclosure of my above-identified U.S. patent application.

(c) On June 28, 2002, Alex King sent an email to Angela Stead and Hugh Preston in which Alex King sought answers to his questions regarding additives and particle size ranges that would be suitable for use in aforesaid Case No. 9861 and in another case identified as Case No. 9707. A copy of Alex King's email is attached hereto as Attachment E.

(d) On August 14, 2002, Alex King sent a note to me with a copy to Angela Stead, to seek answers to several additional technical questions. Electronic copies of an updated draft of an application for my invention and of an inventorship questionnaire were attached to this email. The updated draft patent application is dated August 14, 2002. Copies of this email and of the updated draft patent application and inventorship questionnaire are attached hereto as Attachment F. The disclosure in this updated draft patent application also substantially conforms to the disclosure in my above-identified U.S. patent application.

(e) Later on August 14, 2002, Angela Stead responded to Alex King's email earlier that day. On August 15, 2002, Alex King responded to Angela Stead's email of August 14, 2002. On August 22, 2002, Angela Stead provided additional technical information in an email to Alex King. Copies of this chain of emails are presented in Attachment G hereto.

(f) On October 4, 2002, Alex King sent me an email to which he attached an electronic copy of the "most recent draft" of a patent application for my invention and an inventorship questionnaire. This most recent draft of the patent application is dated August 23, 2002 and also conforms very substantially to my above-identified U.S. patent application. Copies of this email and of this most recent draft of a patent application for my invention are presented in Attachment H. This inventorship questionnaire is identical to the inventorship questionnaire shown in Attachment F.

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(g) On October 14, 2002, Alex King sent an email reminder to me regarding the most recent draft of a patent application for my invention. On November 4, 2002, I emailed Alex King to let him know that I had completed the inventorship questionnaire. A copy of this chain of emails is attached hereto as Attachment I.

(h) On November 15, 2002, U.K. patent application No. 0226726.8 was filed to cover my aforesaid invention. A copy of this U.K. Patent Application and a copy of a certification from The Patent Office of the United Kingdom that the copy of this U.K. Patent is a true copy of the application as filed are attached hereto as Attachment J.

8. Patent Cooperation Treaty patent application No. PCT/GB2003/004855 was filed on November 10, 2003 and was based on and claimed priority from my aforesaid British Patent Application No. 0226726.8. PCT/GB2003/004855 was nationalized in the United States as my above-identified U.S. Patent Application No. 10/535,076 on May 13, 2005.

9. I believe that my above- identified U.S. patent application is entitled to the benefit of the filing date of U.K. patent application No. 0226726.8.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made upon information and belief are believed to be true; and further that any willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of any patent that may issue from this application.

FURTHER DECLARANT SAYETH NOT:

Diane Hall

Diane Elsie Hall

27th January 2010.

Date

ATTACHMENT

A

BP 9861-00 US

REDACTED **Programme Objectives**

Work Programme No: FTS/WP/710-0442/1/01

Objective Group:	Product Development
Objective No/Title:	710-0400/DIESEL EMISSIONS
Element No/Title:	42/Ten ppm Sulphur Fuel
Sponsor(s):	Mkt PG, M&S/SP
Title:	Investigation of the effect of fuel and lubricant sulphur content on the formation of nucleation particles
Research Leader:	D.E.Hall
Author:	Diane E Hall/EUU/BPGroup
Status:	Complete for Sponsor Review

Version: 1.0

Issue Date: REDACTED

It is assumed that, unless the nominated Research Leader hears to the contrary within 21 days of the date c issue (for 'Complete' or 'Revised' documents), the details of the proposed work are acceptable, and the programme will be undertaken as described herein.

1. Purpose:

To examine the effect of fuel and lubricant sulphur on the formation of nucleation particles in the exhaust with and without a CRT fitted.

2. Background/Earlier Work:

Work by CONCAWE (and others) has demonstrated that (using a full flow dilution system), the particle r particles emitted from a HD engine tends to be bimodal. The nature of the size distribution depends on th engine. With the engine operating at high speeds and loads, the distribution consists of a single mode of c the accumulation mode), which stabilise readily and are repeatably measured. At lower speeds/loads whe proportion of unburned hydrocarbon, a second mode appears of smaller (nucleation) particles, which cons hydrocarbons. These particles do not stabilise quickly and are highly susceptible to any variation in samp conditions. These particles are more apparent when the concentration of carbonaceous particles is reduc carbon:hydrocarbon ratio drops. This results in a reduction of available surface for the adsorption of vola consequently forced to self-nucleate.

Although the formation of the nucleation particles is not clearly understood, theory suggests that sulphate normal engine operating conditions the conversion of fuel sulphur to sulphate is not large (2-3%), but in t (especially at higher operating temperatures) the oxidation catalyst increases the sulphate conversion and increased passage of gases through the catalyst (ie no storage) increases the potential for the formation of programme will investigate if there is an influence of the levels of sulphur in the fuel and the lubricant on

3. Cost Allocation:

REDACTED

4. Test Materials & Equipment:

CRT: To be supplied by Johnson Matthey (pre-treatment to be advised by JM)

Engine: Cummins M11 (tested with and without CRT fitted)

Particle size measurement: Measurements will be made from the secondary tunnel using the SMPS (Sca and also the UPM (Ultrafine Particle Monitor). All particle size measurement and basic data analysis wil Technology.

Fuels: 10ppm S meeting EN 590
50ppm S meeting EN 590

Lubes: 'Average' sulphur level
'Low' sulphur - but maintaining same ash levels between fuels

5. Test Procedure:

Fuel/Lube combination.

The following combinations will be tested:

Combination 1 – Low sulphur fuel/low sulphur lube
Combination 2 – Low sulphur fuel/high sulphur lube
Combination 3 – High sulphur fuel/high sulphur lube

Methodology:

Oil Conditioning: 12 hours cycling over the R49 test conditions (the oil may also be conditioned at t depending on the conditioning required for the trap) – samples to be taken of fresh oil, conditioned oil an

test work).

Engine Testing:

Fuel/lube combination 1 (without CRT fitted)

i) Following standard warm-up procedures, two R49 cycles will be run. All regulated emissions me full particle size scans made at each mode to build up a composite distribution. Total particle counts will
ii) One ETC to be run – full emissions measurement and SMPS fixed (approx 15-20nm, based on res will be made with the UPM
iii) Steady state testing – in addition to the scans measured from Modes 6 and 8 during the R49, full s measured at two other speed/load conditions (dependent on engine temperature map and Cummins '8-mo

The conditioned CRT will then be fitted, the engine run for 20 minutes at high temperature and stages i) a period of high speed operation (20 minutes) between each cycle to remove any stored material and to ens CRT operation.

Following the ETC cycle, the engine will then be run again at high speed/high load (or at the highest tem for at least twenty minutes, taking SMPS scans throughout the duration.

For stage iii) steady state testing, three/four modes will now be examined; modes 6 and 8 from the R49 ar identified in iii) above. These modes will be run in decreasing order of temperature and run long enough distribution.

Following an oil change to the high sulphur, this protocol will now be repeated for the other fuel/lube con

6. Milestones/Review Dates:

The test work id due to commence Monday REDACTED will take six days

7. Deliverables:

Full report and data set.

8. Completion Date:

Test work complete REDACTED, report REDACTED

9. Record of Amendments:

10. Technology Review:

Appendix:

ATTACHMENT

B

CONFIDENTIAL

REDACTED Programme Objectives

Work Programme No: FTS/WP/710-0442/1/01

Objective Group:	Product Development
Objective No/Title:	710-0400/DIESEL EMISSIONS
Element No/Title:	42/Ten ppm Sulphur Fuel
Sponsor(s):	Mkt PG, M&S/SP
Title:	Investigation of the effect of fuel and lubricant sulphur content on the formation of nucleation particles from a heavy duty engine
Research Leader:	D.E.Hall
Author:	Diane E Hall/EUU/BPGroup
Status:	Final For Execution

Version: 1.1

Issue Date: REDACTED

It is assumed that, unless the nominated Research Leader hears to the contrary within 21 days of the date of issue (for 'Complete' or 'Revised' documents), the details of the proposed work are acceptable, and the programme will be undertaken as described herein.

1. Purpose:

To examine the effect of fuel and lubricant sulphur on the formation of nucleation particles in the exhaust stream of a HD engine both with and without a CRT fitted.

2. Background/Earlier Work:

Work by CONCAWE (and others) has demonstrated that (using a full flow dilution system), the particle number distribution of particles emitted from a HD engine tends to be bimodal. The nature of the size distribution depends on the operating condition of the engine. With the engine operating at high speeds and loads, the distribution consists of a single mode of carbonaceous particles (called the accumulation mode), which stabilise readily and are repeatably measured. At lower speeds/loads where there is a greater proportion of unburned hydrocarbon, a second mode appears of smaller (nucleation) particles, which consist of condensed sulphate and hydrocarbons. These particles do not stabilise quickly and are highly susceptible to any variation in sampling and measurement conditions. These particles are more apparent when the concentration of carbonaceous particles is reduced and thus the carbon:hydrocarbon ratio drops. This results in a reduction of available surface for the adsorption of volatile species, which are consequently forced to self-nucleate.

Although the formation of the nucleation particles is not clearly understood, theory suggests that sulphate as the initiator. Under normal engine operating conditions the conversion of fuel sulphur to sulphate is not large (2-3%), but in the presence of a CRT (especially at higher operating temperatures) the oxidation catalyst increases the sulphate conversion and this, combined with the increased passage of gases through the catalyst (ie no storage) increases the potential for the formation of the nucleation particles. This programme will investigate if there is an influence of the levels of sulphur in the fuel and the lubricant on nucleation particle formation.

3. Cost Allocation:

REDACTED

4. Test Materials & Equipment:

CRT: To be supplied by Johnson Matthey (pre-treatment to be advised by JM)

Engine: Cummins M11 (tested with and without CRT fitted)

Particle size measurement: Measurements will be made from the secondary tunnel using the SMPS (Scanning Mobility Particle Sizer) and also the UPM (Ultrafine Particle Monitor). All particle size measurement and basic data analysis will be contracted to AEA Technology.

Fuels: 10ppm S meeting EN 590 (GO01/205)

50ppm S meeting EN 590 (GO01/228)

Lubes: 'Average' sulphur level (Valvoline Blue L01/008)
'Low' sulphur - but maintaining same ash levels between fuels (EX-4 ex Castrol)

5. Test Procedure:

Fuel/Lube combination.

The following combinations will be tested:

Combination 1 – Low sulphur fuel/low sulphur lube
Combination 2 – Low sulphur fuel/high sulphur lube
Combination 3 – High sulphur fuel/high sulphur lube

Methodology:

Oil Conditioning: 12 hours cycling over the R49 test conditions (the oil may also be conditioned at the same time as the CRT, depending on the conditioning required for the trap) – samples to be taken of fresh oil, conditioned oil and used oil (at completion of test work).

Engine Testing:

Fuel/lube combination 1 (without CRT fitted)

i) Following standard warm-up procedures, two R49 cycles will be run. All regulated emissions measurements will be made and full particle size scans made at each mode to build up a composite distribution. Total particle counts will be made with the UPM
ii) One ETC to be run – full emissions measurement and SMPS fixed (approx 15-20nm, based on results from R49). Total counts will be made with the UPM
iii) Steady state testing – in addition to the scans measured from Modes 6 and 8 during the R49, full size distributions will be measured at two other speed/load conditions (dependent on engine temperature map and Cummins '8-mode' cycle)

The conditioned CRT will then be fitted, the engine run for 20 minutes at high temperature and stages i) and ii) above repeated, with a

period of high speed operation (20 minutes) between each cycle to remove any stored material and to ensure the same baseline for the CRT operation.

Following the ETC cycle, the engine will then be run again at high speed/high load (or at the highest temperature condition identified) for at least twenty minutes, taking SMPS scans throughout the duration.

For stage iii) steady state testing, three/four modes will now be examined; modes 6 and 8 from the R49 and the two other modes identified in iii) above. These modes will be run in decreasing order of temperature and run long enough to achieve a stable size distribution.

The speed/loads selected are:
1200 r/min - 100%
1400 r/min - 1155Nm
1550 r/min - 1505Nm
1900 r/min - 100%

Following an oil change to the high sulphur, this protocol will now be repeated for the other fuel/lube combinations

6. Milestones/Review Dates:

The test work is due to commence REDACTED and will take.

7. Deliverables:

Full report and data set.

8. Completion Date:

Test work complete end. REDACTED

9. Record of Amendments:

1. The stabilisation period recommended for the test work with the CRT fitted will also be included when the engine is running without it for continuity.
2. The following amendment was made at the end of the programme to verify some observations:

The CRT will be loaded by running mode 7 to 13 of an R49 cycle, then we shall remove the CRT and change to the low sulphur fuel and lubricant mix(G001/205 and AO471C/00B106). The engine will then be stabilised until AEA confirm that the particulate levels are back to original low sulphur values. Once stable the pre loaded CRT will be refitted and another stabilisation will be run to determine if the high number of small particles seen on the higher sulphur fuel-lube tests was influenced by the sampling system, or a result of the CRT.

10. Technology Review:

ATTACHMENT

C

King, Alex

From:	Perkins. Nick D.
Sent:	REDACTED
To:	King, Alex
Subject:	FW: Patent for Sulphur effect on CRT equipped HD engine
Sensitivity:	Confidential

Alex,

Just found this. Hope yuo had it already.

Can yuo put it in the electronic and paper files.

thanks

Nick

-----Original Message-----

From:	Hall. Diane E
Sent:	REDACTED
To:	Perkins, Nick D.
Cc:	Rogerson, John S; Beckwith, Paul
Subject:	Patent for Sulphur effect on CRT equipped HD engine

Nick,

Thank you for your time yesterday. I'm pleased that you think we have a chance to patent this information.

I have attached both the work programme and also the summary results and will check out the confidentiality agreements as promised. I look forward to hearing from you.

Best regards

Diane.

001 Programmes (Lotus).doc

HD nucleation S effects summar...

<u>The effect of fuel sulphur levels on the formation of nucleation particles from trap equipped heavy duty Diesel engines.</u>

Summary

There are two types of particle associated with heavy duty Diesel engine emissions. The first are the accumulation mode particles (generally larger than ~50nm), which are essentially carbonaceous and represent the mass of the particles emitted. The second are nucleation particles (<~50nm), formed by the nucleation of volatile precursors in the exhaust, including sulphates and hydrocarbons. These particles have minimal mass but represent the majority of the number of particles emitted.

As the particle mass emissions from Diesel engines reduce and become harder to measure, so the measurement of particle number as an alternative metric comes under more scrutiny. It has been seen that, as engine technology improves, the total number of emitted particles has increased. This is due to the reduction of the carbonaceous particles (to reduce legislated mass) and thus the removal of available condensation sites. If precursors are not reduced as well, there is potential to increase the nucleation particles, although it must be remembered that the extent of their formation is directly related to the conditions used for their measurement and thus still not an exact science.

The formation of the nucleation particles is exacerbated in the case of a heavy duty engine which has been fitted with a Continuously Regenerating Trap (CRT). In this application, the carbon is totally removed and the operating temperatures are high enough to promote an increase in the precursors for nucleation particles. If one of these precursors is sulphate, then this would be a suitable condition to use to investigate the effect of fuel (and lubricant) sulphur on the formation of nucleation particles.

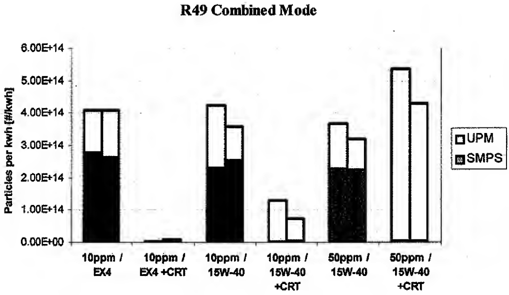
Test work has been completed which has compared this formation potential from 10ppm S fuel versus 50ppm S fuel and also examined (with the 10ppm S fuel) any potential contribution from the lubricant sulphur. The attached graph shows the results in numbers of particles emitted/kWh from a Euro II engine running over the legislated R49 cycle.

The six pairs of results show repeats of:

- Low sulphur lube/low sulphur fuel without CRT
- Low sulphur lube/low sulphur fuel with CRT
- High sulphur lube/low sulphur fuel without CRT
- High sulphur lube/low sulphur fuel with CRT
- High sulphur lube/high sulphur fuel without CRT
- High sulphur lube/high sulphur fuel with CRT

In each case the coloured bar represents the total number of particle measured by the SMPS (Scanning Mobility Particle Sizer) within a specified size range and the clear bar represents the total number of particles >3nm as measured by a particle counter (Ultrafine Particle Monitor). Thus any difference between the two bars represents

particles outside the scan range of the SMPS and in this case, those particle between 3 and 7 nm (nucleation particles)



This graph clearly demonstrates firstly the effectiveness of the trap at removing particles and secondly that changing both fuel and lubricant sulphur has implications for the formation of the nucleation particles *under these operating conditions.*

Reduction of fuel sulphur levels from 50ppm to 10ppm S clearly reduces the concentration of precursors for the formation of nucleation particles.

ATTACHMENT

D

King, Alex

From: King, Alex
Sent: 20 May 2002 09:19
To: Hall, Diane E
Subject: Case 9861 - draft first filing

Diane,

Please find attached a draft of the first filing. I have highlighted some parts in red, either because it would be useful to have further detail or because I have made assumptions on preferred embodiments which may not be appropriate (at least some of the text is taken from the related cases we have and may not be valid).

Please check through the whole document and check that you are happy with the technical content. Please give me a call or send back any corrections when you have had a chance to have a look.

Many thanks

Alex

9861(1) draft.doc
(Compressed)...

CONFIDENTIAL

DRAFT
FIRST FILING

Case No: 9861 (1)

Title: LUBRICATING OIL

Applicant: BP Oil International Limited – to be confirmed

Inventors: Not yet determined

Please circulate the patent specification without delay and return to Patents & Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex, TW16 7LN.

Please check the facts described in the specification; that the examples contain sufficient information to enable them to be repeated; and that the specification describes the **best method known** to you of carrying out the invention.

If the invention involves the use of any information from the USA, or if any person outside BP Amoco or in a different BP Group Company has been involved in making the invention, please ensure that Patents & Agreements are informed.

If you are aware of any information or publications which may have a bearing on the patentability of the application, you are under a continuing obligation to inform Patents & Agreements and, if possible supply a copy.

For distribution To	Information From		Signature	Date
	USA Yes/No	Person Outside Your BP Company Yes/No		
Diane Hall				

Date: 3 April. 2002

Section titles are for guidance only and will be removed prior to filing.

LUBRICATING OIL

Field of the Invention.

The present invention relates to the use of a lube oil with low sulphur content with a low sulphur fuel to reduce particulate emissions of a diesel engine.

Discussion of the Prior Art and its Disadvantages.

Diesel engines are commonly used on private and commercial vehicles, particularly on commercial vehicles such as buses and lorries. It is known that emissions from diesel engines may comprise carbon oxides, nitrogen oxides, sulphur oxides, hydrocarbons and particulates. It is desirable to reduce these emissions either as a whole or individually. Whilst some of the emissions have their origin in the fuel which is combusted in the engine, the lubricating oil which is used to lubricate the engine can also impact on the tail-pipe emissions, for example by direct emission of combustion products or by affecting the catalyst/trap performance.

For example, the particulate emissions from an engine are believed to be related, at least in part, to the sulphur content of the fuel. Thus, there has been a trend in recent years to reduce sulphur content of internal combustion fuels.

Despite the trend towards low sulphur fuels, with the advent of increasingly stringent particulate emissions controls in many areas of the world, for example, in the EU and USA, such as the particulate emissions limits for vehicles within city limits in states such as California, and states in the north-east of the USA, many diesel vehicles must now be fitted with particulate traps.

Although particulate traps may significantly reduce the total mass of particulate emissions, the majority of the particulates removed by the trap are relatively large, agglomeration particles. However, although making up a relatively low proportion of the total mass of particulate emissions, it has been found that a significant number of the total particulates emitted are relatively smaller, nucleation particles. Particulate traps are less efficient at removing these smaller, nucleation particles from the emissions. Therefore, whilst the agglomeration particles have a significant contribution to the total mass of the particles in the emissions, the very small nucleation particles are the more significant with respect to health issues, since they may penetrate deep into lungs.

We have now surprisingly found that the level of nucleation particle emissions from a diesel engine may be significantly decreased by use of a low sulphur lube with a low sulphur fuel in diesel engines fitted with a particulate trap.

Statement of the Invention – Broad Definition.

Thus according to the present invention there is provided the use of a low sulphur lube oil in combination with a low sulphur diesel fuel to reduce the emissions of nucleation particles from a diesel engine fitted with a particulate trap.

It has been found that use of a low sulphur lube with a low sulphur fuel according to the present invention causes significantly reduced nucleation particulate emissions compared to use of a conventional lube with a low sulphur fuel. Surprisingly the reduction in nucleation particulate emissions is significantly larger than would be expected based on the reduction in sulphur level of the lube oil alone.

Thus, according to another embodiment of the present invention there is provided a method of reducing the number of nucleation particles in the emissions from a diesel engine fitted with a particulate trap, which method comprises using a low sulphur content lubricating oil and a low sulphur fuel.

Description of Preferred Embodiments.

The present invention is particularly useful wherein the particulate trap is a continuously regenerating trap (CRT).

The diesel engine may be any suitable diesel engine but is preferably a heavy duty diesel engine.

The nucleation particles may have a diameter in the range of from 1 nm to 30 nm inclusive, preferably in the range from 3nm to 20nm inclusive, and most preferably in the range from 5 nm to 15 nm inclusive.

The low sulphur fuel preferably has a sulphur content below 100ppm, such as below 50ppm. More preferably the sulphur content of the fuel is below 20ppm, and most preferably is 10ppm or lower.

The low sulphur lube oil preferably has a sulphur content of less than 0.4%, such as less than 0.3%. More preferably the lube oil has a sulphur content of less than 0.2%, and most preferably less than 0.15%.

A known additive used in lubricating oils for lubricating diesel engines engine is zinc dialkyl dithiophosphate (ZDDP). This is used as an anti-wear and anti-oxidant additive. However, this additive contains sulphur. Therefore according to another aspect of the present invention there is provided a lubricating oil for use in an internal combustion engine which has a ZDDP content at most 0.6% by weight, preferably at most 0.3% by weight, and more preferably is substantially free of ZDDP.

The lubricating oil according to the present invention may comprise one or more anti-wear additives which might be used, at least in part, to replace ZDDP, such as anti-wear additives selected from the group consisting of (a) molybdenum containing compounds, such as MoDTC, **[Is MoDTC a good example ? any other examples, what does MoDTC stand for]** (b) organic based friction modifiers, such as oleamides **[any others]**, and (c) salicylate-type detergents **[examples ?]**.

The lubricating oil according to the present invention may comprise one or more anti-oxidant additives which might be used, at least in part, to replace ZDDP. Preferably at least one of the anti-oxidant additives may be selected from the group consisting of aminic or phenolic compounds, such as **[example ?]**.

The lubricating oil according to the present invention may comprise one or more other additives which may be known to one skilled in the art as lubricating oil additives. Such additives may include one or more of anti-foam additives, Viscosity Index improvers and dispersants

Examples.

Tests were performed on a Heavy Duty (HD) diesel engine **(– 11l (2l/cyl), TC/IC, electronic FIE – please explain these terms, can we define the engine more accurately e.g. make/model)**

(do we have commercial brand name, specifications or model numbers for any of the fuels, the conventional lube oil, trap or particle analysers ?)

Two different fuels were tested. The low sulphur fuel (Fuel 1) comprised 10ppm sulphur. The high sulphur fuel (Fuel 2) comprised a sample of fuel 1, doped to 50ppm sulphur.

Two lubricants were tested. The first was a conventional ("high sulphur") lube oil comprising 0.75wt% sulphur, supplied by Castrol. The second was a low sulphur lube oil comprising 0.12wt% sulphur

Tests were performed both with and without a Continuously Regenerating Trap (CRT), supplied by Johnson Matthey.

Particle size measurement was made with both a standard Scanning Mobility Particle Sizer (SMPS) (scanning between 7-320nm), and an Ultrafine Particulate Monitor (UPM) (giving total particle count >3nm)

Tests were performed under the EC Reg. 49 testing conditions. This is one of the standard regulatory tests for emissions that diesel engines in Europe ?? may have to pass, depending, for example, on the age of the engine and the fuel type. Other tests include the European Steady-state Cycle (ESC) test and the European Transient Cycle (ETC) test,

The R49 test requires the engine to be tested in numerous "modes" based on different steady-state operating conditions. The emissions in each mode may be

measured and aggregated according to a defined mathematical formula to give a "combined mode" result. For particle emissions the standard test method measures the mass of particles produced in each mode. The combined mode result therefore gives an aggregated total mass of particles produced per kWh of power.

In the examples given the total number of particulate emissions was measured using both a standard Scanning Mobility Particle Sizer (SMPS) (scanning between 7-320nm), and an Ultrafine Particulate Monitor (UPM) (giving total particle count >3nm). These results were then aggregated to give a combined mode particle emission value in number of particles per kWh.

For comparison, Figure 1 gives the particle emissions measured as particle mass (in g/kWh) according to the standard EC Reg. 49 test, for combinations of the low and high sulphur fuels (LSF and HSF), and the low and high sulphur lube oils (LSL and HSL), in the presence and absence of the CRT.

It can be seen that in the absence of a CRT the emissions, in terms if particle mass, are approximately similar, and actually increase slightly for the low sulphur lube with the low sulphur fuel. This may be expected since in the absence of the trap only a small proportion of the sulphur in the fuel is emitted as particulates, and the changes in sulphur level will have only a small impact on regulated emissions. However in the presence of the CRT the total mass of particles produced is more dependent on the sulphur level and reduces as the sulphur level is decreased.

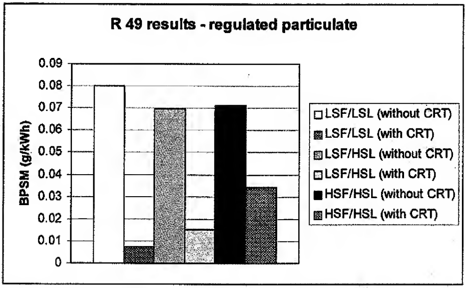


Figure 1: R 49 regulated particulate emissions by mass (g/kWh).

Figure 2 shows the data for total particle emission rates (/kWh) for the 10ppm and 50ppm sulphur fuels with the two lubricants measured using both SPMS and UPM. The two bars for each set represent repeat experiments showing high reproducibility.

The shaded bars represent the SMPS measurement and the clear bars represent the UPM measurement, the difference between the coloured bars and the open bars being the small particles detected by the UPM (but not the SMPS).

It can be seen that with the 50ppm sulphur fuel and high sulphur lube oil in the presence of the trap (CRT) then essentially all the agglomeration particles are removed from the emissions, but a larger number of nucleation particles are emitted compared to the test in the absence of the CRT. This increase is, at least in part, due to reaction of sulphur dioxide on the oxidation catalyst in the CRT to produce sulphates, which are emitted from the CRT under the conditions in certain modes of the R49 test.

For a low sulphur fuel with the high sulphur lube oil it can be seen that in the absence of a trap the total particle emissions are very similar to those for the high sulphur fuel, as may be expected by comparison with figure 1. Again this is due to the fact that in the absence of the trap only a small proportion of the sulphur in the fuel is emitted as particulates. In the presence of a trap, essentially all of the agglomeration particles are

removed from the emissions, as seen for the high sulphur fuel. In this case the total number of nucleation particles produced decreases compared to the high sulphur fuel, but are similar to the numbers of nucleation particles seen in the absence of the trap.

For the low sulphur lube oil with a low sulphur fuel the emissions in the absence of the CRT are again similar to those seen for the experiments with the high sulphur lube oil and the low sulphur and high sulphur fuels respectively, as expected. However the use of a low sulphur lube with a low sulphur petrol in the presence of the CRT, according to the present invention, leads to total particulate emissions that are very significantly lower than expected based on the reduction in the sulphur level.

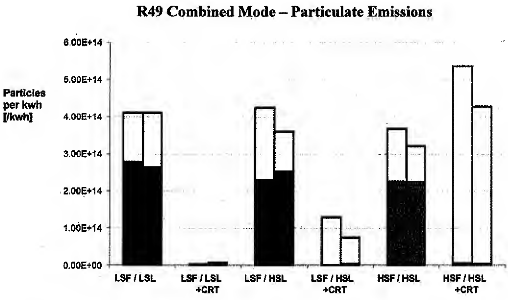


Figure 2: R49 Combined mode total particulate emissions (/kWh) measured by SPMS (shaded areas) and UPM (open areas).

SAMPLE CLAIMS – NOT NECESSARILY FOR FILING

Claims

1. The use of a low sulphur lube oil in combination with a low sulphur diesel fuel to reduce the emissions of nucleation particles from a diesel engine fitted with a particulate trap.

2. A use according to claim 1 wherein the low sulphur lube has a sulphur content of at most 0.20 % by weight.

3. A use according to claim 1 or claim 2 wherein the low sulphur diesel has a sulphur content of at most 20ppm by weight.

4. A use according to any one of the preceding claims wherein the low sulphur lube comprises at most 0.6% by weight ZDDP.

5. A use according to claim 4 wherein the low sulphur lube is substantially free of ZDDP.

6. A use according to any one of the preceding claims wherein the low sulphur lube further comprises one or more anti-wear additives selected from the group consisting of (a) molybdenum containing compounds, (b) organic based friction modifiers, and (c) salicylate-type detergents.

7. A use according to any one of the preceding claims wherein the low sulphur lube further comprises one or more anti-oxidant additives selected from the group consisting of [*?????*].

8. A use according to any one of the preceding claims wherein the low sulphur lube further comprises one or more additives selected from the group consisting of [***??? - what classes of additive are used and what examples of each class ?***]

9. A use according to any one of the preceding claims wherein the very small nucleation particles have a diameter in the range of from 10 nm to 20 nm inclusive, preferably in the range from 12 nm to 14 nm inclusive.

10. A use according to any one of the preceding claims wherein the diesel engine is a heavy duty diesel engine.

11. A method of reducing the number of nucleation particles in the emissions from a diesel engine fitted with a particulate trap, which method comprises using a low sulphur content lubricating oil in combination with a low sulphur fuel as claimed in any one of claims 1 to 10.

ATTACHMENT

E

King, Alex

From: King, Alex
Sent: 28 June 2002 14:28
To: Stead, Angela L; Preston, Hugh
Cc: Hall, Diane E; Pearse, Steven; Warrens, Chris P
Subject: Patents cases

Angela, Hugh (and/or Steve and Chris if you can help)

Diane Hall and I have been working on a draft of a patent application (our ref: 9861) related to the use of a low sulphur lube in combination with a low sulphur fuel in a diesel engine fitted with a particulate trap to reduce particulate emissions.

Could you please help with the following questions on this and the 2 related cases:

All 3 cases that I am currently working on discuss removal of ZDDP as an additive. Can anyone give me any specific information on the types of additives that will be used to replace the ZDDP in terms of both anti-wear and anti-oxidation properties. This is what I have at present:

The lubricating oil according to the present invention may comprise one or more anti-wear additives which might be ed, at least in part, to replace ZDDP, such as anti-wear additives selected from the group consisting of (a) molybdenum containing compounds, such as MoDTC, [Is MoDTC a good example ? any other examples, what does MoDTC stand for] (b) organic based friction modifiers, such as oleamides [any others], and (c) salicylate-type detergents [examples ?].

The lubricating oil according to the present invention may comprise one or more anti-oxidant additives which might be used, at least in part, to replace ZDDP. Preferably at least one of the anti-oxidant additives may be selected from the group consisting of aminic or phenolic compounds, such as [example ?].

Both 9707 and 9861 discuss nucleation particles. However both analyse particles in different size ranges. Is it possible to agree on a broad technical definition of the particle size range for nucleation particles, say 1 to 30nm that I can use in both applications ? (Note that this doesn't affect the respective ranges over which the inventions are illustrated)

Finally, the low sulphur lubricating oil in 9861 was, I understand, supplied by Castrol (ref: EX4, 0.12% sulphur). Can anyone please give any other details as to the origin of this lube, and in particular if it or any part of it was supplied by a third party to Castrol or whether it was developed in-house ? Also, if possible, what types of additive did it contain to replace ZDDP ?

.hank you in advance for your responses. In addition if anyone has any additional comments on the current drafts of their respective applications please let me know. Nick has suggested that he and I arrange a visit to Pangbourne in the near future to try and finalise these applications. Can I start by suggesting one of 17/18/22/23 July. I note that the patents seminar is 30th July, but I am not sure whether we would have time on that day.

Regards

Alex

Dr Alex King
Trainee Patent Attorney
bp Sunbury
853 63207

ATTACHMENT

F

Perkins, Nick D.

From: King, Alex
Sent: 14 August 2002 10:11
To: Hall, Diane E
Cc: Stead, Angela L
Subject: Case 9861

Attachments: 9861(1) draft140802.doc (Compressed); 9861IQ.doc

Diane,

Thanks for your call and apologies again for the delay on this case.
I have updated the draft below based on our discussions in late June and the details from Castrol regarding the additives that may be used to replace ZDDP.

We still need to know more about the low sulphur lube (Ex. 4) supplied to you, for example how much ZDDP and at least the chemical types of other additives present. **(Angela - have you had any joy finding out about this ?)**

If possible do we have a make or reference for the conventional lube oil used as well ?

Finally can we find out the make/model of the two particle sizers used (though probably not essential) ?

Can you also please fill out the inventorship questionaire below.

If there are any questions or further comments please let me know.

Thanks

Alex

9861(1) draft140802.doc

9861IQ.doc

CONFIDENTIAL

DRAFT
FIRST FILING

Case No: 9861 (1)

Title: LUBRICATING OIL

Applicant: BP Oil International Limited – to be confirmed

Inventors: Not yet determined

Please circulate the patent specification without delay and return to Patents & Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex, TW16 7LN.

Please check the facts described in the specification; that the examples contain sufficient information to enable them to be repeated; and that the specification describes the **best method known** to you of carrying out the invention.

If the invention involves the use of any information from the USA, or if any person outside BP Amoco or in a different BP Group Company has been involved in making the invention, please ensure that Patents & Agreements are informed.

If you are aware of any information or publications which may have a bearing on the patentability of the application, you are under a continuing obligation to inform Patents & Agreements and, if possible supply a copy.

For distribution To	Information From		Signature	Date
	USA Yes/No	Person Outside Your BP Company Yes/No		
Diane Hall				

Date: 14th August 2002

Section titles are for guidance only and will be removed prior to filing.

LUBRICATING OIL

Field of the Invention.

The present invention relates to lubricating oils, and in particular to the use of lubricating oils with low sulphur content in combination with a low sulphur fuel to reduce particulate emissions of a diesel engine equipped with a catalysed diesel particulate filter.

Discussion of the Prior Art and its Disadvantages.

Diesel engines are commonly used on private and commercial vehicles, particularly on commercial vehicles such as buses and lorries. It is known that emissions from diesel engines may comprise carbon oxides, nitrogen oxides, sulphur oxides, hydrocarbons and particulates. It is desirable to reduce these emissions either as a whole or individually. Whilst some of the emissions have their origin in the fuel which is combusted in the engine, the lubricating oil which is used to lubricate the engine can also impact on the tail-pipe emissions, for example by direct emission of combustion products of the oil or by affecting the catalyst/trap performance.

In particular, the particulate emissions from an engine are believed to be related, at least in part, to the sulphur content of the fuel. Thus, in addition to the benefit lower sulphur gives to after-treatment devices, there has been a trend in recent years to reduce sulphur content of internal combustion fuels.

Despite the trend towards low sulphur fuels, with the advent of increasingly stringent particulate emissions controls in many areas of the world, for example, in the EU and USA, such as the particulate emissions limits for vehicles within city limits in states such as California, and states in the north-east of the USA, there may be a requirement for diesel vehicles to be fitted with particulate traps.

Particulate traps or filters have been shown to be effective at trapping particles formed in the combustion process. During the combustion process, and especially in the presence of an oxidation catalyst in a catalysed particulate filter or trap, a percentage of the sulphur in the fuel forms sulphates. Where a particulate trap is present the majority of this should remain in the particulate trap. However, under certain operating conditions, where the temperature of the trap becomes elevated, this material is released and, along with volatile emissions that now come straight through the trap, can condense after the trap to produce large numbers of nucleation particles.

These, relatively small, nucleation particles typically have a diameter in the range of from 1 nm to 30 nm inclusive, and although making up a relatively low mass of particulate emissions, it has been found that these nucleation particles can make a significant contribution to the total number of particulates emitted.

It is desirable to reduce the number of these particles emitted.

We have now surprisingly found that the level of nucleation particle emissions from a diesel engine fitted with a particulate trap may be significantly decreased by use of a low sulphur lube in combination with a low sulphur fuel.

Statement of the Invention – Broad Definition.

Thus according to the present invention there is provided the use of a low sulphur lube oil in combination with a low sulphur diesel fuel to reduce the emissions of nucleation particles from a diesel engine fitted with a particulate trap.

It has been found that use of a low sulphur lube with a low sulphur fuel according to the present invention causes significantly reduced nucleation particulate emissions compared to use of a conventional lube with a low sulphur fuel. Surprisingly

the reduction in nucleation particulate emissions is significantly larger than might be expected based on the reduction in sulphur level of the lube oil alone.

Thus, according to another embodiment of the present invention there is provided a method of reducing the number of nucleation particles in the emissions from a diesel engine fitted with a particulate trap, which method comprises using a low sulphur content lubricating oil in combination with a low sulphur content diesel fuel.

Description of Preferred Embodiments.

The present invention is particularly useful wherein the particulate trap is a catalysed particulate trap, which comprises both an oxidation catalyst and a filter. An example of such a trap is a continuously regenerating trap (CRT™). In the combustion of a fuel the majority of any sulphur present is converted to sulphur dioxide, with a relatively small amount, typically 1-2%, being converted to sulphates. These sulphates may act as precursors for particulate formation. In the presence of a particulate filter, but the absence of an oxidation catalyst, the gas formed from combustion of the fuel (and lube) contacts the filter, which will remove at least some of the particles formed from the gas. However the trapped particles may quickly block the filter, and to burn the particles off (as CO_2) requires very high temperatures, not normally reached in the trap. In a catalysed particulate trap, as well as the filter there is also provided an oxidation catalyst. The gas first contacts the oxidation catalyst, wherein, for example, components such as sulphur dioxide in the gas are oxidised to sulphates. The oxidised gas then contacts the filter, which can trap the particulates. In a continuously regenerating trap, at least some of the particulates trapped are burnt off from the filter by reaction with oxidation products from the catalyst, such as nitrogen dioxide (which is formed by oxidation of NO_x species in the combustion gas). These reactions occur at lower temperatures than those that would otherwise be required to burn the particulates off, and at temperatures that can be reached in the traps fitted to diesel engines, and hence the trap is continuously regenerated.

The diesel engine may be any suitable diesel engine but is preferably a heavy duty diesel engine.

The low sulphur fuel preferably has a sulphur content below 100ppm, such as below 50ppm. More preferably the sulphur content of the fuel is below 20ppm, and most preferably is 10ppm or lower.

The low sulphur lube oil preferably has a sulphur content of less than 0.4%, such as less than 0.3%. More preferably the lube oil has a sulphur content of less than 0.2%, and most preferably less than 0.15%.

A known additive used in lubricating oils for lubricating diesel engines engine is zinc dialkyl dithiophosphate (ZDDP). This is used as an anti-wear, anti-oxidant and corrosion inhibitor additive. However, this additive contains sulphur. Therefore according to another aspect of the present invention there is provided a lubricating oil for use in an internal combustion engine which has a ZDDP content at most 0.6% by weight, preferably at most 0.3% by weight, and more preferably is substantially free of ZDDP.

The lubricating oil according to the present invention may comprise one or more anti-wear additives which might be used, at least in part, to replace ZDDP, such as anti-wear additives selected from the group consisting of (a) molybdenum containing compounds, such as molybdenum dithiocarbamate (MoDTC), molybdenum dithiophosphate and molybdenum amines (b) organic based friction modifiers, such as oleamides, acids, amines, alcohols, phosphate esters and glycerol monooleates, and (c) salicylate-type detergents, such as calcium salicylate and magnesium salicylate.

The lubricating oil according to the present invention may comprise one or more anti-oxidant additives which might be used, at least in part, to replace ZDDP. Preferably at least one of the anti-oxidant additives may be selected from the group consisting of aromatic amines or phenolic compounds, such as hindered phenols.

The lubricating oil according to the present invention may comprise one or more corrosion inhibitor additives which might be used, at least in part, to replace ZDDP. Preferably the corrosion inhibitor additives may be selected from conventional non-sulphur detergent additives.

The lubricating oil according to the present invention may comprise one or more other additives which may be known to one skilled in the art as lubricating oil additives.

Such additives may include one or more of anti-foam additives, Viscosity Index improvers and dispersants.

Examples.

Tests were performed on a Heavy Duty (HD) diesel engine (11litre (2l/cyl), turbo-charged/intercooled diesel engine fitted with electronic fuel injection equipment)

Two different fuels were tested. Fuel 1 was a low sulphur fuel comprising 10ppm sulphur and corresponding to EN-590 specification. Fuel 2 was a high sulphur fuel and was produced by doping a sample of fuel 1 to 50ppm sulphur.

Two lubricants were tested. The first was a conventional lube oil comprising 0.75wt% sulphur, supplied by Castrol, herein designated as "high sulphur". The second was a low sulphur lube oil comprising 0.12wt% sulphur. (EX4 supplied by Castrol)

Tests were performed both with and without a Continuously Regenerating Trap (CRT^{TM}), supplied by Johnson Matthey.

Particle size measurement was made with both a standard (make) Scanning Mobility Particle Sizer (SMPS) (scanning between 7-320nm), and an (make) Ultrafine Particulate Monitor (UPM) (giving total particle count >3nm)

Tests were performed under the EC Reg. 49 testing conditions. For engines built prior to 2000 this is the standard homologation test for heavy duty diesel engines in Europe.

The R49 test cycle requires the engine to be tested in numerous "modes" based on different steady-state operating conditions. The emissions in each mode are measured and aggregated according to a regulated procedure to give a single result for the cycle. For particle emissions the standard test method measures the mass of particles produced in each mode. The result therefore gives an aggregated total mass of particles produced per kWh of power.

In the examples given the total number of particulate emissions was measured using both a standard Scanning Mobility Particle Sizer (SMPS) (scanning between 7-320nm), and an Ultrafine Particulate Monitor (UPM) (giving total particle count >3nm). These results were then aggregated to give a combined mode particle emission value for

the R49 cycle in number of particles per kWh. The aggregation was performed in the same manner as for the regulated procedure for mass of particulate emissions the R49 test.

For comparison, Figure 1 gives the particle emissions measured as particle mass (in g/kWh) according to the standard EC Reg. 49 test, for combinations of the low and high sulphur fuels (LSF and HSF), and the low and high sulphur lube oils (LSL and HSL), in the presence and absence of the CRT™.

It can be seen that in the absence of a CRT™ the emissions, in terms if particle mass, are approximately similar, and actually increase slightly for the low sulphur lube with the low sulphur fuel. This may be expected since in the absence of the trap only a small proportion of the sulphur in the fuel is emitted as particulates, and the changes in sulphur level will have only a small impact on regulated emissions. However in the presence of the CRT™, due to the presence of the oxidation catalyst, the total mass of particles produced is more dependent on the sulphur levels in the lube and fuel and reduces as the sulphur levels in the lube and fuel are decreased.

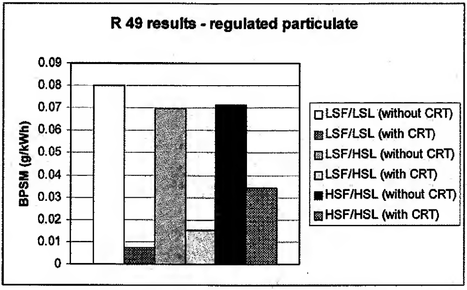


Figure 1: R 49 regulated particulate emissions by mass (g/kWh).

Figure 2 shows the data for total particle emission rates (/kWh) for the 10ppm and 50ppm sulphur fuels with the two lubricants measured using both SPMS and UPM. The two bars for each set represent repeat experiments showing high reproducibility.

The shaded bars represent the SMPS measurement and the clear bars represent the UPM measurement, the difference between the coloured bars and the open bars being the small particles detected by the UPM (but not the SMPS) i.e. nucleation particles of between about 3 and 7 nm diameter.

It can be seen that with the 50ppm sulphur fuel and high sulphur lube oil then essentially all the agglomeration particles are removed from the emissions by the presence of the trap (CRT^{TM}), but a larger number of nucleation particles are emitted compared to the test in the absence of the CRT^{TM}. This increase is, at least in part, due to reaction of sulphur dioxide on the oxidation catalyst in the CRT^{TM} to produce sulphates, which are emitted from the CRT^{TM} under the conditions in certain modes of the R49 test.

For a low sulphur fuel with the high sulphur lube oil it can be seen that in the absence of a trap the total particle emissions are very similar to those for the high sulphur fuel, as may be expected by comparison with Figure 1. Again this is due to the fact that in the absence of the trap only a small proportion of the sulphur in the fuel is emitted as particulates. In the presence of a trap, essentially all of the agglomeration particles are removed from the emissions, as seen for the high sulphur fuel. In this case the total number of nucleation particles produced decreases compared to the high sulphur fuel.

For the low sulphur lube oil with a low sulphur fuel the emissions in the absence of the CRT^{TM} are again similar to those seen for the experiments with the high sulphur lube oil and the low sulphur and high sulphur fuels respectively, as expected. However the use of a low sulphur lube with a low sulphur fuel in the presence of the CRT^{TM} gives total particulate emissions that are very significantly lower than expected based on the reduction in the sulphur level.

In particular the use of a low sulphur lube oil in combination with a low sulphur diesel fuel leads to a reduction in the emissions of nucleation particles from a diesel engine fitted with a particulate trap.

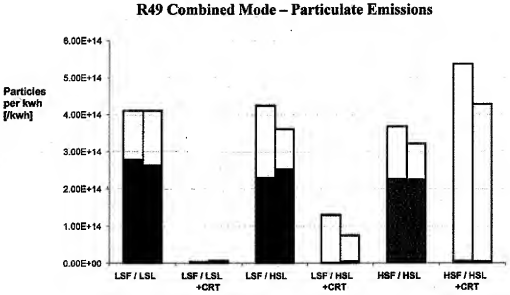


Figure 2: R49 Combined mode total particulate emissions (/kWh) measured by SPMS (shaded areas) and UPM (open areas).

SAMPLE CLAIMS – NOT NECESSARILY FOR FILING

Claims

1. The use of a low sulphur lube oil in combination with a low sulphur diesel fuel to reduce the emissions of nucleation particles from a diesel engine fitted with a particulate trap.

2. A use according to claim 1 wherein the low sulphur lube has a sulphur content of at most 0.20 % by weight.

3. A use according to claim 1 or claim 2 wherein the low sulphur diesel has a sulphur content of at most 20ppm by weight.

4. A use according to any one of the preceding claims wherein the low sulphur lube comprises at most 0.6% by weight ZDDP.

5. A use according to claim 4 wherein the low sulphur lube is substantially free of ZDDP.

6. A use according to any one of the preceding claims wherein the low sulphur lube further comprises one or more anti-wear additives selected from the group consisting of (a) molybdenum containing compounds, such as molybdenum dithiocarbamate (MoDTC), molybdenum dithiophosphate and molybdenum amines (b) organic based friction modifiers, such as oleamides, acids, amines, alcohols, phosphate esters and glycerol monooleates, and (c) salicylate-type detergents, such as calcium salicylate and magnesium salicylate.

7. A use according to any one of the preceding claims wherein the low sulphur lube further comprises one or more anti-oxidant additives selected from the group consisting of aromatic amines or phenolic compounds, such as hindered phenols.

8. A use according to any one of the preceding claims wherein the low sulphur lube further comprises one or more additives selected from the group consisting of corrosion inhibitor additives, anti-foam additives, Viscosity Index improvers and dispersants

9. A use according to any one of the preceding claims wherein the diesel engine is a heavy duty diesel engine.

10. A method of reducing the number of nucleation particles in the emissions from a diesel engine fitted with a particulate trap, which method comprises using a low sulphur content lubricating oil in combination with a low sulphur fuel as claimed in any one of claims 1 to 10.

PATENT CASE NO. 9861

QUESTIONNAIRE ON INVENTORSHIP

In order to safeguard the rights of inventors and the Company when making a patent application, it is important to name the legally correct inventor(s). If you have contributed, either to the conception of the invention or its subsequent development, PLEASE COMPLETE, SIGN AND THEN RETURN THIS QUESTIONNAIRE THROUGH YOUR MANAGER TO GROUP PATENTS AND AGREEMENTS.

Please note that the statements made may require future verification on oath.

---

1. The invention in this case relates in general to

the use of a low sulphur lube oil in combination with a low sulphur diesel fuel to reduce the emissions of nucleation particles from a diesel engine fitted with a particulate trap.

2. Please give details of <u>your</u> contribution to the invention defined above and/or its practical development. Dates, first records, laboratory notebook references and other relevant circumstances must be given if available.

3. When was the invention tried out in practice (give date, place, scale, laboratory notebook references etc.) and by whom?

4. Name anyone, whether Company employee or not, apart from those named above, who may have contributed to the invention and/or its development. Please give details of the contribution if known. Do not leave this blank. If to the best of your knowledge no other person has contributed, please state accordingly.

5. Please state which BP Company employed you at the time of your contribution to the invention. If you were not employed by a BP Company, what was your relationship with BP ?

6. Does this case fall within the terms of any proposed or existing Agreement?

Signed ....

*Full names (please print)...

*Current Home Address...

....

*Job Title.................................... *Nationality ....

<u>Witness</u>:

Signed.................................... Occupation.....................

Date....................................

* This information may be required in order to complete the necessary legal formalities.

Only one copy of this questionnaire should be completed by each person who may have contributed to this invention or its subsequent development.

ATTACHMENT

G

King, Alex

From: Stead, Angela L
Sent: 22 August 2002 09:25
To: King, Alex
Subject: RE: Case 9861

Alex,

The ZDDP in EX4 is in the formulation at a concentration to give 0.04% P. In a normal commercial lube the ZDDP is in the formulation at a concentration to give 0.12% P.

Let me know if you need anymore info.

Regards,

Angela

-----Original Message-----
From: King, Alex
Sent: 15 August 2002 14:58
To: Stead, Angela L
Subject: RE: Case 9861

Angela,

Thanks for this - do you know approximately how much the ZDDP has been reduced by compared to a conventional lube oil and the percentage by weight of ZDDP in the lube ?

Alex

-----Original Message-----
From: Stead, Angela L
Sent: 14 August 2002 12:01
To: King, Alex; Hall, Diane E
Subject: RE: Case 9861

Alex,

Here are the details I have found out for you about EX 4. It is basically a low S, low P and low Sulfated Ash heavy duty diesel formulation - Exact levels are given below:

S	0.143%
P	0.038%
SA	0.74%

It is a synthetic 5W30 formulation. To achieve low S and P they have reduced the ZDDP and used oleamide as a supplementary antiwear component. To achieve the low ash level they have reduced the ash containing detergent and increased the amount of low Mwt dispersant to compensate for the drop in TBN.

I hope this information is useful. Don't hesitate to contact me if you need more details.

Best regards,

Angela

-----Original Message-----
From: King, Alex
Sent: 14 August 2002 10:11
To: Hall, Diane E
Cc: Stead, Angela L
Subject: Case 9861

Diane,

Thanks for your call and apologies again for the delay on this case.
I have updated the draft below based on our discussions in late June and the details from Castrol regarding the additives that may be used to replace ZDDP.

We still need to know more about the low sulphur lube (Ex. 4) supplied to you, for example how much ZDDP and at least the chemical types of other additives present. **(Angela - have you had any joy finding out about this ?)**

If possible do we have a make or reference for the conventional lube oil used as well ?

Finally can we find out the make/model of the two particle sizers used (though probably not essential) ?

Can you also please fill out the inventorship questionaire below.

If there are any questions or further comments please let me know.

Thanks

Alex

<< File: 9861(1) draft140802.doc (Compressed) >> << File: 9861IQ.doc >>

ATTACHMENT

H

Perkins, Nick D.

From: King, Alex
Sent: 14 October 2002 12:52
To: Hall, Diane E
Subject: FW: Case 9861(1) - reminder

Attachments: 9861(1) draft041002.doc (Compressed); 9861IQ.doc

Diane,

Just a further reminder. Any questions or problems please let me know.

Thanks

Alex

-----Original Message-----
From: King, Alex
Sent: 04 October 2002 14:13
To: Hall, Diane E
Subject: Case 9861(1) - reminder

Diane,

Just a reminder that this case has yet to be filed. I attach below the most recent copy which includes all the details from Pangbourne of the low sulphur lube oil (EX4). Please check that you are happy to file this.
I also attach another copy of the inventorship questionnaire. Could you please fill in a copy of this, and forward a copy to anyone else who may have been involved with the invention. We will need to address inventorship before we can file.

Nick has also asked me to confirm that this case can, in future, be charged to budget number 600-2034 (which corresponds to OTC-710-1300 since I understand that it shouldn't be charged to the consumer/commercial budget it has previously.

If you have any questions please let me know.
Many thanks

Alex

9861(1) draft041002.doc

9861IQ.doc

CONFIDENTIAL

DRAFT
FIRST FILING

Case No: 9861 (1)

Title: LUBRICATING OIL

Applicant: BP Oil International Limited – to be confirmed

Inventors: Not yet determined

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For distribution To	Information From		Signature	Date
	USA Yes/No	Person Outside Your BP Company Yes/No		
Diane Hall				

Date: 23rd August 2002

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LUBRICATING OIL

Field of the Invention.

The present invention relates to lubricating oils, and in particular to the use of lubricating oils with low sulphur content in combination with a low sulphur fuel to reduce particulate emissions of a diesel engine equipped with a particulate trap.

Discussion of the Prior Art and its Disadvantages.

Diesel engines are commonly used on private and commercial vehicles, particularly on commercial vehicles such as buses and lorries. It is known that emissions from diesel engines may comprise carbon oxides, nitrogen oxides, sulphur oxides, hydrocarbons and particulates. It is desirable to reduce these emissions either as a whole or individually. Whilst some of the emissions have their origin in the fuel which is combusted in the engine, the lubricating oil which is used to lubricate the engine can also impact on the tail-pipe emissions, for example by direct emission of combustion products of the oil or by affecting the trap performance.

In particular, the particulate emissions from an engine are believed to be related, at least in part, to the sulphur content of the fuel. Thus, in addition to the benefit lower sulphur gives to after-treatment devices, there has been a trend in recent years to reduce sulphur content of internal combustion fuels.

Despite the trend towards low sulphur fuels, with the advent of increasingly stringent particulate emissions controls in many areas of the world, for example, in the

EU and USA, such as the particulate emissions limits for vehicles within city limits in states such as California, and states in the north-east of the USA, there may be a requirement for diesel vehicles to be fitted with particulate traps.

Particulate traps have been shown to be effective at trapping particles formed in the combustion process. During the combustion process, and especially in the presence of an oxidation catalyst in a catalysed particulate trap, a percentage of the sulphur in the fuel forms sulphates. Where a particulate trap is present the majority of this should remain in the particulate trap. However, under certain operating conditions, where the temperature of the trap becomes elevated, this material is released and, along with volatile emissions that now come straight through the trap, can condense after the trap to produce large numbers of nucleation particles.

These, relatively small, nucleation particles typically have a diameter in the range of from 1 nm to 30 nm inclusive, and although making up a relatively low mass of particulate emissions, it has been found that these nucleation particles can make a significant contribution to the total number of particulates emitted.

It is desirable to reduce the number of these particles emitted.

We have now surprisingly found that the level of nucleation particle emissions from a diesel engine fitted with a particulate trap may be significantly decreased by use of a low sulphur lube in combination with a low sulphur fuel.

Statement of the Invention – Broad Definition.

Thus according to the present invention there is provided the use of a low sulphur lube oil in combination with a low sulphur diesel fuel to reduce the emissions of nucleation particles from a diesel engine fitted with a particulate trap.

It has been found that use of a low sulphur lube with a low sulphur fuel according to the present invention causes significantly reduced nucleation particulate emissions compared to use of a conventional lube with a low sulphur fuel. Surprisingly the reduction in nucleation particulate emissions is significantly larger than might be expected based on the reduction in sulphur level of the lube oil alone.

Thus, according to another embodiment of the present invention there is provided a method of reducing the number of nucleation particles in the emissions from a diesel engine fitted with a particulate trap, which method comprises using a low sulphur content lubricating oil in combination with a low sulphur content diesel fuel.

Description of Preferred Embodiments.

The present invention is particularly useful wherein the particulate trap is a catalysed particulate trap, which comprises both an oxidation catalyst and a filter. An example of such a trap is a continuously regenerating trap (CRT™). In the combustion of a fuel the majority of any sulphur present is converted to sulphur dioxide, with a relatively small amount, typically 1-2%, being converted to sulphates. These sulphates may act as precursors for particulate formation. In the presence of a particulate filter, but the absence of an oxidation catalyst, the gas formed from combustion of the fuel (and lube) contacts the filter, which will remove at least some of the particles formed from the gas. However the trapped particles may quickly block the filter, and to burn the particles off (as CO_2) requires very high temperatures, not normally reached in the trap. In a catalysed particulate trap, as well as the filter there is also provided an oxidation catalyst. The gas first contacts the oxidation catalyst, wherein, for example, components such as sulphur dioxide in the gas are oxidised to sulphates. The oxidised gas then contacts the filter, which can trap the particulates. In a continuously regenerating trap, at least some of the particulates trapped are burnt off from the filter by reaction with oxidation products from the catalyst, such as nitrogen dioxide (which is formed by oxidation of NO_x species in the combustion gas). These reactions occur at lower temperatures than those that would otherwise be required to burn the particulates off, and at temperatures that can be reached in the traps fitted to diesel engines, and hence the trap is continuously regenerated.

The diesel engine may be any suitable diesel engine but is preferably a heavy duty diesel engine.

The low sulphur fuel preferably has a sulphur content below 100ppm (by weight), such as below 50ppm. More preferably the sulphur content of the fuel is below 20ppm, and most preferably is 10ppm or lower.

The low sulphur lube oil preferably has a sulphur content of less than 0.4%, such as less than 0.3%. More preferably the lube oil has a sulphur content of less than 0.2%, and most preferably less than 0.15%.

A known additive used in lubricating oils for lubricating diesel engines engine is zinc dialkyl dithiophosphate (ZDDP). This is used as an anti-wear, anti-oxidant and corrosion inhibitor additive. However, this additive contains sulphur. Therefore according to another aspect of the present invention there is provided a lubricating oil for use in an internal combustion engine which has a ZDDP content at most 0.8% by weight, preferably at most 0.4% by weight, and more preferably is substantially free of ZDDP.

The lubricating oil according to the present invention may comprise one or more anti-wear additives which might be used, at least in part, to replace ZDDP, such as anti-wear additives selected from the group consisting of (a) molybdenum containing compounds, such as molybdenum dithiocarbamate (MoDTC), molybdenum dithiophosphate and molybdenum amines (b) organic based friction modifiers, such as oleamides, acids, amines, alcohols, phosphate esters and glycerol monooleates, and (c) salicylate-type detergents, such as calcium salicylate and magnesium salicylate.

The lubricating oil according to the present invention may comprise one or more anti-oxidant additives which might be used, at least in part, to replace ZDDP. Preferably at least one of the anti-oxidant additives may be selected from the group consisting of aromatic amines or phenolic compounds, such as hindered phenols.

The lubricating oil according to the present invention may comprise one or more corrosion inhibitor additives which might be used, at least in part, to replace ZDDP. Preferably, the corrosion inhibitor additives may be selected from conventional non-sulphur detergent additives.

The lubricating oil according to the present invention may comprise one or more other additives which may be known to one skilled in the art as lubricating oil additives.

Such additives may include one or more of anti-foam additives, Viscosity Index improvers and dispersants.

Examples.

Tests were performed on a Heavy Duty (HD) diesel engine (11litre (2l/cyl), turbo-charged/intercooled diesel engine fitted with electronic fuel injection equipment)

Two different fuels were tested. Fuel 1 was a low sulphur fuel comprising 10ppm sulphur and corresponding to EN-590 specification. Fuel 2 was a high sulphur fuel and was produced by doping a sample of fuel 1 to 50ppm sulphur.

Two lubricants were tested. The first was a conventional lube oil comprising 0.75wt% sulphur, supplied by Castrol, herein designated as "high sulphur". The second was a low sulphur synthetic based SAE 5W-30 lube oil comprising 0.14wt% sulphur, in which the ZDDP level was reduced compared to the conventional lube oil, to give a ZDDP level of 0.38wt%, and oleamide was added as an additional antiwear additive.

Tests were performed both with and without a Continuously Regenerating Trap (CRT™), supplied by Johnson Matthey.

Particle size measurement was made with both a standard Scanning Mobility Particle Sizer (SMPS) (scanning between 7-320nm), and an Ultrafine Particulate Monitor (UPM) (giving total particle count >3nm)

Tests were performed under the EC Reg. 49 testing conditions. For engines built prior to 2000 this is the standard homologation test for heavy duty diesel engines in Europe. The R49 test cycle requires the engine to be tested in numerous "modes" based on different steady-state operating conditions. The emissions in each mode are measured and aggregated according to a regulated procedure to give a single result for the cycle. For particle emissions the standard test method measures the mass of particles produced in each mode. The result therefore gives an aggregated total mass of particles produced per kWh of power.

In the examples given, the total number of particulate emissions was measured using both a standard Scanning Mobility Particle Sizer (SMPS) (scanning between 7-320nm),

and an Ultrafine Particulate Monitor (UPM) (giving total particle count >3nm). These results were then aggregated to give a combined mode particle emission value for the R49 cycle in number of particles per kWh. The aggregation was performed in the same manner as for the regulated procedure for mass of particulate emissions the R49 test.

For comparison, Figure 1 gives the particle emissions measured as particle mass (in g/kWh) according to the standard EC Reg. 49 test, for combinations of the low and high sulphur fuels (LSF and HSF), and the low and high sulphur lube oils (LSL and HSL), in the presence and absence of the CRT™.

It can be seen that in the absence of a CRT™ the emissions, in terms of particle mass, are approximately similar, and actually increase slightly for the low sulphur lube with the low sulphur fuel. This may be expected since in the absence of the trap only a small proportion of the sulphur in the fuel is emitted as particulates, and the changes in sulphur level will have only a small impact on regulated emissions. However in the presence of the CRT™, due to the presence of the oxidation catalyst, the total mass of particles produced is more dependent on the sulphur levels in the lube and fuel and reduces as the sulphur levels in the lube and fuel are decreased.

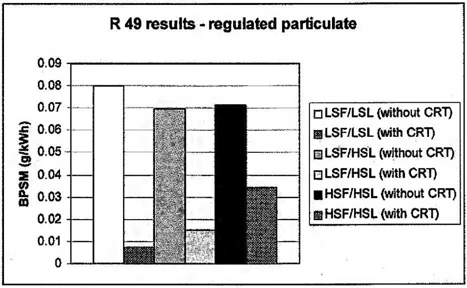

Figure 1: R 49 regulated particulate emissions by mass (g/kWh).

Figure 2 shows the data for total particle emission rates (/kWh) for the 10ppm and 50ppm sulphur fuels with the two lubricants measured using both SPMS and UPM. The two bars for each set represent repeat experiments showing high reproducibility. The shaded bars represent the SMPS measurement and the clear bars represent the UPM measurement, the difference between the shaded bars and the open bars being the small particles detected by the UPM (but not the SMPS) i.e. nucleation particles of between about 3 and 7 nm diameter.

It can be seen that with the 50ppm sulphur fuel and high sulphur lube oil then essentially all the agglomeration particles are removed from the emissions by the presence of the trap (CRT™), but a larger number of nucleation particles are emitted compared to the test in the absence of the CRT™. This increase is, at least in part, due to reaction of sulphur dioxide on the oxidation catalyst in the CRT™ to produce sulphates, which are emitted from the CRT™ under the conditions in certain modes of the R49 test.

For a low sulphur fuel with the high sulphur lube oil it can be seen that in the absence of a trap the total particle emissions are very similar to those for the high sulphur fuel, as may be expected by comparison with Figure 1. Again this is due to the fact that in the absence of the trap only a small proportion of the sulphur in the fuel is emitted as particulates. In the presence of a trap, essentially all of the agglomeration particles are removed from the emissions, as seen for the high sulphur fuel. In this case the total number of nucleation particles produced decreases compared to the high sulphur fuel.

For the low sulphur lube oil with a low sulphur fuel the emissions in the absence of the CRT™ are again similar to those seen for the experiments with the high sulphur lube oil and the low sulphur and high sulphur fuels respectively, as expected. However the use of a low sulphur lube with a low sulphur fuel in the presence of the CRT™ gives total particulate emissions that are very significantly lower than expected based on the reduction in the sulphur level.

In particular the use of a low sulphur lube oil in combination with a low sulphur diesel fuel leads to a reduction in the emissions of nucleation particles from a diesel engine fitted with a particulate trap.

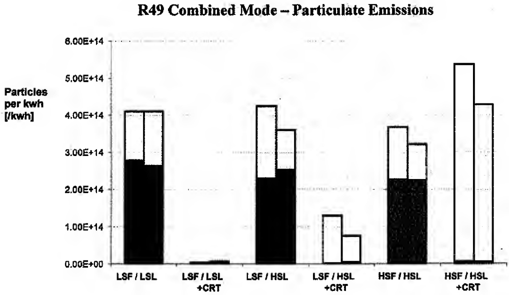

Figure 2: R49 Combined mode total particulate emissions (/kWh) measured by SPMS (shaded areas) and UPM (open areas).

SAMPLE CLAIMS – NOT NECESSARILY FOR FILING

Claims

1. The use of a low sulphur lube oil in combination with a low sulphur diesel fuel to reduce the emissions of nucleation particles from a diesel engine fitted with a particulate trap.

2. A use according to claim 1 wherein the low sulphur lube has a sulphur content of at most 0.20 % by weight.

3. A use according to claim 1 or claim 2 wherein the low sulphur diesel has a sulphur content of at most 20ppm by weight.

4. A use according to any one of the preceding claims wherein the low sulphur lube comprises at most 0.6% by weight ZDDP.

5. A use according to claim 4 wherein the low sulphur lube is substantially free of ZDDP.

6. A use according to any one of the preceding claims wherein the low sulphur lube further comprises one or more anti-wear additives selected from the group consisting of (a) molybdenum containing compounds, such as molybdenum dithiocarbamate (MoDTC), molybdenum dithiophosphate and molybdenum amines (b) organic based friction modifiers, such as oleamides, acids, amines, alcohols, phosphate esters and glycerol monooleates, and (c) salicylate-type detergents, such as calcium salicylate and magnesium salicylate.

7. A use according to any one of the preceding claims wherein the low sulphur lube further comprises one or more anti-oxidant additives selected from the group consisting of aromatic amines or phenolic compounds, such as hindered phenols.

8. A use according to any one of the preceding claims wherein the low sulphur lube further comprises one or more additives selected from the group consisting of corrosion inhibitor additives, anti-foam additives, Viscosity Index improvers and dispersants

9. A use according to any one of the preceding claims wherein the diesel engine is a heavy duty diesel engine.

10. A method of reducing the number of nucleation particles in the emissions from a diesel engine fitted with a particulate trap, which method comprises using a low sulphur content lubricating oil in combination with a low sulphur fuel as claimed in any one of claims 1 to 10.

ATTACHMENT

I

King, Alex

From: Hall, Diane E
Sent: 04 November 2002 09:36
To: King, Alex
Subject: FW: Case 9861(1) - reminder

Alex,

I have filled in the questionnaire as requested (but not very well I feel!). I had hoped to attach a link to the work programme in Lotus Notes but have been unable to master the technology required (and I am not sure that the link would work unless you have access to our fuels database anyway). Consequently, I have appended the WP, but it has played havoc with the formatting. I hope you can still deal with the document.

I know that this also sounds stupid - but I am not sure as to my parent company - whether it is BP Oil or BP Oil International. I believe that Patents are the right people to ask for the 'legal' wording...so over to you!

Finally, your file note looks OK with the following amendments:
Point 2 - basic analysis of raw particle size data and preparation of graphs carried out by AEA Technology. Graphic presentation of regulated emissions results prepared by AEI Consulting.
Point 5 - 'Consultant' replaced with 'AEI Consulting'. Didn't actually suggest any modifications to the R49 itself (it's a legislated test) but rather to the daily test protocol, which enabled better repeatability and control of the engine.
Point 6 - 'AEA' should be 'AEA Technology'. Also as point 2 - all data work up and graph preparation done by them.

And, yes - the results have been presented to both Cummins and JM, under a 'strictly confidential' banner.

Please come back to me if any of this isn't clear or if I have mucked up your questionnaire too much to be useful!

Again, apologies for the delay.

Best regards

Diane.

-----Original Message-----
From: King, Alex
Sent: 14 October 2002 12:52
To: Hall, Diane E
Subject: FW: Case 9861(1) - reminder

Diane,

Just a further reminder. Any questions or problems please let me know.

Thanks

Alex

-----Original Message-----
From: King, Alex
Sent: 04 October 2002 14:13
To: Hall, Diane E

Subject: Case 9861(1) - reminder

Diane,

Just a reminder that this case has yet to be filed. I attach below the most recent copy which includes all the details from Pangbourne of the low sulphur lube oil (EX4). Please check that you are happy to file this.
I also attach another copy of the inventorship questionnaire. Could you please fill in a copy of this, and forward a copy to anyone else who may have been involved with the invention. We will need to address inventorship before we can file.

Nick has also asked me to confirm that this case can, in future, be charged to budget number 600-2034 (which corresponds to OTC-710-1300 since I understand that it shouldn't be charged to the consumer/commercial budget it has previously.

If you have any questions please let me know.
Many thanks

Alex

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9861IQ.doc

ATTACHMENT

J

The Patent Office

INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
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South Wales
NP10 8QQ

REC'D 16 DEC 2003
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In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed Stephen Hordley

Dated 28 November 2003

Patents Form 1/77

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P01/7700 0.00-0226726.8

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(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference

9861

2. Patent application number
(The Patent Office will fill in this part)

15 NOV 2002

0226726.8

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

BP OIL INTERNATIONAL LIMITED
BRITANNIC HOUSE
1 FINSBURY CIRCUS
LONDON
LONDON
EC2M 7BA
UNITED KINGDOM

06396552001.
Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

METHOD

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

PERKINS, Nicholas David
BP INTERNATIONAL LIMITED
PATENTS & AGREEMENTS
CHERTSEY ROAD
SUNBURY-ON-THAMES
MIDDLESEX
TW16 7LN
UNITED KINGDOM

Patents ADP number *(if you know it)* 05904107001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*
   a) any applicant named in part 3 is not an inventor, or
   b) there is an inventor who is not named as an applicant, or
   c) any named applicant is a corporate body.
   See note (d))

YES

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	
Description	7
Claim(s)	–
Abstract	–
Drawing(s)	–

RM

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*

Request for preliminary examination and search *(Patents Form 9/77)*

Request for substantive examination *(Patents Form 10/77)*

Any other documents *(please specify)*

11\. I/We request the grant of a patent on the basis of this application.

Signature Date 15.11.2002

PERKINS, Nicholas David

12. Name and daytime telephone number of person to contact in the United Kingdom (01932) 763214

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

a) *If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.*

b) *Write your answers in capital letters using black ink or you may type them.*

c) *If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*

d) *If you have answered 'Yes' Patents Form 7/77 will need to be filed.*

e) *Once you have filled in the form you must remember to sign and date it.*

f) *For details of the fee and ways to pay please contact the Patent Office.*

METHOD

The present invention relates to lubricating oils, and in particular to the use of lubricating oils with low sulphur content in combination with a low sulphur fuel to reduce particulate emissions of a diesel engine equipped with a particulate trap.

Diesel engines are commonly used on private and commercial vehicles, particularly on commercial vehicles such as buses and lorries. It is known that emissions from diesel engines may comprise carbon oxides, nitrogen oxides, sulphur oxides, hydrocarbons and particulates. It is desirable to reduce these emissions either as a whole or individually. Whilst some of the emissions have their origin in the fuel which is combusted in the engine, the lubricating oil which is used to lubricate the engine can also impact on the tail-pipe emissions, for example by direct emission of combustion products of the oil or by affecting the trap performance.

In particular, the particulate emissions from an engine are believed to be related, at least in part, to the sulphur content of the fuel. Thus, in addition to the benefit lower sulphur gives to after-treatment devices, there has been a trend in recent years to reduce sulphur content of internal combustion fuels.

Despite the trend towards low sulphur fuels, with the advent of increasingly stringent particulate emissions controls in many areas of the world, for example, in the EU and USA, such as the particulate emissions limits for vehicles within city limits in states such as California, and states in the north-east of the USA, there may be a requirement for diesel vehicles to be fitted with particulate traps.

Particulate traps have been shown to be effective at trapping particles formed in the combustion process. During the combustion process, and especially in the presence

of an oxidation catalyst in a catalysed particulate trap, a percentage of the sulphur in the fuel forms sulphates. Where a particulate trap is present the majority of this should remain in the particulate trap. However, under certain operating conditions, where the temperature of the trap becomes elevated, this material is released and, along with volatile emissions that now come straight through the trap, can condense after the trap to produce large numbers of nucleation mode particles.

These, extremely small, nucleation mode particles typically have a diameter in the range of from 1 nm to 30 nm inclusive. Although larger carbonaceous particles (accumulation mode particles) make up the majority of the mass of particulate emissions, whilst the nucleation mode particles make up a relatively low mass of particulate emissions, it has been found that these nucleation mode particles can make a significant contribution to the total number of particulates emitted.

It is thus desirable to reduce the number of these nucleation particles emitted.

We have now surprisingly found that the concentration of nucleation mode particle emissions from a diesel engine fitted with a particulate trap may be significantly decreased by use of an engine lubricating oil having a low sulphur content (low sulphur lube oil) in combination with a fuel having a low sulphur content (low sulphur fuel).

Thus, according to the present invention there is provided the use of an engine lubricating oil having a low sulphur content in combination with a fuel having a low sulphur content, to reduce the emissions of nucleation mode particles from a diesel engine fitted with a particulate trap.

It has been found that use of a low sulphur lube oil with a low sulphur fuel according to the present invention causes significantly reduced nucleation mode particulate emissions compared to use of a conventional lube oil with a low sulphur fuel. Surprisingly the reduction in nucleation mode particulate emissions is significantly larger than might be expected based on the reduction in sulphur level of the lube oil alone.

Thus, according to another embodiment of the present invention there is provided a method of reducing the number of nucleation mode particles in the emissions from a diesel engine fitted with a particulate trap, which method comprises using an engine lubricating oil having a low sulphur content in combination with a fuel having a low sulphur content.

The present invention is particularly useful wherein the particulate trap is a catalysed particulate trap, which comprises both an oxidation catalyst and a filter. An example of such a trap is a continuously regenerating trap (CRT[TRADE MARK]). In the combustion of a fuel the majority of any sulphur present is converted to sulphur dioxide, with a relatively small amount, typically 1-2%, being converted to sulphates. These sulphates may act as precursors for particulate formation. In the presence of a particulate filter, but the absence of an oxidation catalyst, the gas formed from combustion of the fuel (and lube oil) contacts the filter, which will remove at least some of the particles formed from the gas. However the trapped particles may quickly block the filter, and to burn the particles off (as CO_2) requires very high temperatures, not normally reached in the trap. In a catalysed particulate trap, as well as the filter there is also provided an oxidation catalyst. The gas first contacts the oxidation catalyst, wherein, for example, components such as sulphur dioxide in the gas are oxidised to sulphates. The oxidised gas then contacts the filter, which can trap the particulates. In a continuously regenerating trap, at least some of the particulates trapped are burnt off from the filter by reaction with oxidation products from the catalyst, such as nitrogen dioxide (which is formed by oxidation of NO_x species in the combustion gas). These reactions occur at lower temperatures than those that would otherwise be required to burn the particulates off, and at temperatures that can be reached in the traps fitted to diesel engines, and hence the trap is continuously regenerated. However, sulphates are not burned off, but are re-volatilised at high temperatures, thus providing the potential to re-form as particles post-trap.

The diesel engine may be any suitable diesel engine but is preferably a heavy duty diesel engine.

The low sulphur fuel preferably has a sulphur content below 100ppm (by weight), such as below 50ppm. More preferably the sulphur content of the fuel is below 20ppm, and most preferably is 10ppm or lower.

The low sulphur lube oil preferably has a sulphur content of less than 0.4% (by weight), such as less than 0.3%. More preferably the lube oil has a sulphur content of less than 0.2%, and most preferably less than 0.15%.

A known additive used in lubricating oils for lubricating diesel engines engine is zinc dialkyl dithiophosphate (ZDDP). This is used as an anti-wear, anti-oxidant and

corrosion inhibitor additive. However, this additive contains sulphur. Therefore according to another aspect of the present invention the lubricating oil has a ZDDP content at most 0.8% by weight, preferably at most 0.4% by weight, and more preferably is substantially free of ZDDP.

The lubricating oil may comprise one or more anti-wear additives which might be used, at least in part, to replace ZDDP, such as anti-wear additives selected from the group consisting of (a) molybdenum containing compounds, such as molybdenum dithiocarbamate (MoDTC), molybdenum dithiophosphate and molybdenum amines (b) organic based friction modifiers, such as oleamides, acids, amines, alcohols, phosphate esters and glycerol monooleates, and (c) salicylate-type detergents, such as calcium salicylate and magnesium salicylate.

The lubricating oil may comprise one or more anti-oxidant additives which might be used, at least in part, to replace ZDDP. Preferably at least one of the anti-oxidant additives may be selected from the group consisting of aromatic amines or phenolic compounds, such as hindered phenols.

The lubricating oil may comprise one or more corrosion inhibitor additives which might be used, at least in part, to replace ZDDP. Preferably, the corrosion inhibitor additives may be selected from conventional non-sulphur detergent additives.

The lubricating oil may comprise one or more other additives which may be known to one skilled in the art as lubricating oil additives. Such additives may include one or more of anti-foam additives, Viscosity Index improvers and dispersants.

<u>Examples.</u>

Tests were performed on a Heavy Duty (HD) diesel engine (11litre (2l/cyl), turbo-charged/intercooled diesel engine fitted with electronic fuel injection equipment)

Two different fuels were tested. Fuel 1 was a low sulphur fuel comprising 10ppm sulphur and corresponding to EN-590 specification. Fuel 2 was a high sulphur fuel and was produced by doping a sample of fuel 1 to 50ppm sulphur.

Two lubricants were tested. The first was a conventional lube oil comprising 0.75wt% sulphur, supplied by Castrol, herein designated as "high sulphur". The second was a low sulphur synthetic based SAE 5W-30 lube oil comprising 0.14wt% sulphur, in which the ZDDP level was reduced compared to the conventional lube oil, to give a ZDDP level of 0.38wt%, and oleamide was added as an additional antiwear additive.

Tests were performed both with and without a Continuously Regenerating Trap (CRT), supplied by Johnson Matthey.

Particle size measurement was made with both a TSI 3071 Scanning Mobility Particle Sizer (SMPS) (scanning between 7-320nm), and a Booker Systems Ultrafine Particulate Monitor (UPM) (giving total particle count >3nm)

Tests were performed under the ECE Reg. 49 testing conditions. For engines built prior to 2000 this is the standard homologation test for heavy duty diesel engines in Europe.

The R49 test cycle requires the engine to be tested over 13 steady-state modes at based at different speed/load operating conditions. The emissions in each mode are measured and aggregated according to a regulated procedure to give a single result for the cycle. For particle emissions the standard test method measures the mass of particles produced in each mode. The result therefore gives an aggregated total mass of particles produced per kWh of power.

In the examples given, the total number of particulate emissions was measured using both a standard Scanning Mobility Particle Sizer (SMPS) (scanning between 7-320nm), and an Ultrafine Particulate Monitor (UPM) (giving total particle count >3nm). These results were then aggregated to give a combined mode particle emission value for the R49 cycle in number of particles per kWh. The aggregation was performed in the same manner as for the regulated procedure for mass of particulate emissions the R49 test.

For comparison, Figure 1 gives the particle emissions measured as particle mass (in g/kWh) according to the standard ECE Reg. 49 test, for combinations of the low and high sulphur fuels (LSF and HSF), and the low and high sulphur lube oils (LSL and HSL), in the presence and absence of the CRT.

It can be seen that in the absence of a CRT the emissions, in terms of particle mass, are approximately similar. Significant changes in mass emission in the absence of the trap would not be expected as only a small proportion of the sulphur in the fuel is emitted as particulates, and the changes in sulphur level will have only a small impact on regulated emissions. However in the presence of the CRT, due to the presence of the oxidation catalyst, the total mass of particles produced is more dependent on the sulphur levels in the lube oil and fuel and reduces as the sulphur levels in the lube oil and fuel

are decreased.

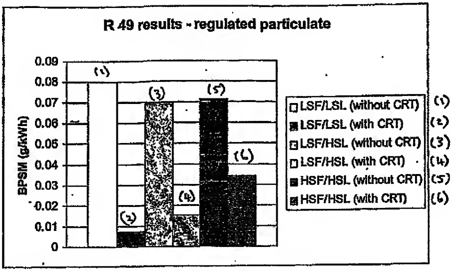

Figure 1: R 49 regulated particulate emissions by mass (g/kWh).

Figure 2 shows the data for total particle emission rates (number/kWh) for the 10ppm and 50ppm sulphur fuels with the two lubricants measured using both SPMS and UPM. The two bars for each set represent repeat experiments showing high reproducibility.

The shaded bars represent the SMPS measurement and the clear bars represent the UPM measurement, the difference between the shaded bars and the open bars being the small particles detected by the UPM (but not the SMPS) i.e. nucleation mode particles of between about 3 and 7 nm diameter.

It can be seen that with the 50ppm sulphur fuel and high sulphur lube oil then essentially all the accumulation mode particles are removed from the emissions by the presence of the trap (CRT), but a larger number of nucleation mode particles are emitted compared to the test in the absence of the CRT. This increase is, at least in part, due to reaction of sulphur dioxide on the oxidation catalyst in the CRT to produce sulphates, which are emitted from the CRT under the conditions in certain modes of the R49 test.

For a low sulphur fuel with the high sulphur lube oil it can be seen that in the absence of a trap the total particle emissions are very similar to those for the high sulphur fuel, as may be expected by comparison with Figure 1. Again this is due to the fact that in the absence of the trap only a small proportion of the sulphur in the fuel is emitted as particulates. In the presence of a trap, essentially all of the accumulation

mode particles are removed from the emissions, as seen for the high sulphur fuel. In this case the total number of nucleation mode particles produced decreases compared to the high sulphur fuel.

For the low sulphur lube oil with a low sulphur fuel the emissions in the absence of the CRT are again similar to those seen for the experiments with the high sulphur lube oil and the low sulphur and high sulphur fuels respectively, as expected. However the use of a low sulphur lube oil with a low sulphur fuel in the presence of the CRT gives total particulate emissions that are very significantly lower than expected based on the reduction in the sulphur level.

In particular the use of a low sulphur lube oil in combination with a low sulphur diesel fuel leads to a reduction in the emissions of nucleation mode particles from a diesel engine fitted with a particulate trap.

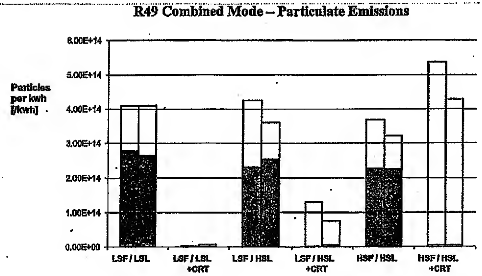

Figure 2: R49 Combined mode total particulate emissions (number/kWh) measured by SPMS (shaded areas) and UPM (open areas).